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16. ABSTRACT

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Characterization of the Aerosol in the Great Smoky Mountains

Robert K. Stevens,* Thomas G. Dzubay, Robert W. Shaw, Jr., William A. McClenny, Charles W. Lewis, and William E. Wilson

Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711

■ A 6-day field study was conducted in the Great Smoky Mountains to measure the composition of the aerosol that pervades this region. Sampling was performed with three dichotomous samplers, a mobile laboratory containing instruments to measure gaseous pollutants, and two gas chromatographs for measuring halocarbons. Sulfate and its associated cations represented 61% of the particle mass. The average ionic composition of the SO_4^{2-}, H^+, and NH_4^+ was equivalent to ammonium bisulfate. Of the total mass measured in the fine particles, elemental carbon accounted for 5% and organic carbon accounted for 10%. Crustal elements such as aluminum, calcium, iron, and silica were minor constituents of the fine-particle mass. During the period of the study the fine-particle aerosol in the Great Smoky Mountains was dominated not by natural organic compounds but by acid sulfates.

Introduction

Went (*1*) in 1960 suggested that blue haze, which is often seen in rural areas on sunny days, is due to fine-particle aerosol produced in photochemical reactions of natural, volatile organic emissions from plants and trees. Since 1960, investigators (*2–4*) have discovered that plants and trees do, in fact, emit a variety of volatile organics and have concluded that natural organic vapors may contribute significantly to formation of aerosols. Some controversy still exists concerning the relative contributions of natural and anthropogenic organic compounds to aerosols and decreased visibility. In studies to characterize air masses passing over several rural locations—a pine forest in North Carolina, citrus groves in Florida, and portions of the Everglades—Bufalini and coworkers (*5, 6*) found that the gaseous samples were dominated by volatile organics normally associated with automotive emissions, rather than natural emissions. Their study may indicate that anthropogenic pollution pervades forested areas in the eastern United States and overshadows pollution from biogenic sources.

The above studies were mainly concerned with measurements of organic aerosol precursors in the gas phase. More recently, Weiss et al. (*7*) studied aerosol composition directly at a rural site in the Ozark Mountains. They concluded that the haze in the Ozark Mountains was caused not by natural organic compounds, but by sulfate aerosol particles. The authors did not quantitatively measure the composition of the aerosol but used a nephelometer with variable humidification to infer the presence of various forms of aerosol sulfate. Pierson et al. (*8*) collected aerosols at a remote site on a forested mountain area in Pennsylvania during 17 days in the summer of 1977. The dominant chemical feature of the aerosol was the stoichiometric balance of the anion SO_4^{2-} with the cations NH_4^+ and H^+, with H^+ being the more abundant cation when sulfate levels exceeded 12 $\mu g/m^3$. Sulfate and its associated H^+, NH_4^+, and water constituted nearly all of the aerosol mass, with SO_4^{2-} alone constituting as much as 50% of the aerosol mass. The H^+ and SO_4^{2-} levels, with sizes concentrated in the light-scattering region (mass median equivalent diameter = 0.84 μm for each species), were proportional to the atmospheric light-scattering coefficient b_{scat} (correlation coefficients r = 0.88 and 0.90, respectively) and inversely related to visual range. Sulfate was not correlated to SO_2 or trace metals. The carbon content of the aerosol was small, averaging only 6% of the SO_4^{2-} concentration.

The studies cited above represent two opposing views of the dominant chemical components in aerosol in rural areas—natural organic vs. sulfate—and consequently suggest the need for a further coordinated effort to characterize both the gases and the aerosols in a forested area relatively distant from multiple anthropogenic sources. As an initial step in addressing this problem, a field study was conducted to test a variety of new techniques for aerosol characterization and to determine which instrumentation and analysis methods may be most useful in understanding the origin and composition of atmospheric haze. The field study was conducted in the Great Smoky Mountains National Park from September 20 to 26, 1978. The experiment consisted of collection and analysis of aerosols, and gas-phase analysis for CO, NO, NO_2, SO_2, O_3, halocarbons, SF_6, HNO_3, and C_2–C_{10} organic compounds.

Aerosols were collected so that their elemental and ionic composition could be determined. Two additional aerosol experiments were carried out: one to measure gaseous and particulate nitrate in a manner that permits correction for sampling artifacts, and one to determine the extent, if any, of artifact formation on glass fiber filters. Gas measurements were chosen to aid in determining whether the sampled air was representative of natural or anthropogenic sources. The rationale was as follows: (a) halocarbons, CO, NO_x and sulfur gases indicate intrusion of air from anthropogenic sources; (b) CO and NO_x are associated with emissions from automobiles; (c) halocarbons are expected to be associated with population density (F-11, F-12) and possibly air conditioned automobiles (F-12) but not power plants except where considerable use of refrigeration occurs; and (d) sulfur gases indicate intrusion from fossil fuel combustion activities. Measurements of gaseous organic compounds were made to determine the possible contribution of biogenic hydrocarbon emissions to aerosols. An aircraft passing over the study site took several measurements of O_3 and SO_2 and made aerosol collections.

Experimental Procedure

Measurements were made in a northern portion of the Great Smoky Mountains National Park near the Elkmont campground, at 35° 40′ N and 83° 36′ W. This location is 10 km southwest of Gatlinburg, TN, and 40 km southeast of Knoxville, TN. The site elevation at Elkmont is 646 m, and the elevation of mountain peaks located to the southeast and east is 2000 m. The site is surrounded on all sides by forest, which is a wilderness for 30 km to the south.

Measurements were made in the center of a 45 × 55 m clearing in the forest. About 30 m to the east was a small river, and about 60 m to the east was a lightly traveled road that carried automobile traffic to a camping area located about 1 km to the south. Although a precise traffic count was not made during the study, we estimate that, on the average, fewer than 10 vehicles per hour passed the site. Equipment at the site included four aerosol samplers and a mobile laboratory containing instruments to measure gaseous pollutants. An additional aerosol sampler for collecting organic compounds and two gas chromatographs for measuring halocarbons were also operated, and the results will be reported separately (*9*). Electrical power was brought in on a transmission line.

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Table I. Instruments for Measuring Gaseous Pollutants

pollutant	instrument	monitoring method	calibration procedure
sulfur dioxide (SO_2)	Meloy Mdl 285	flame photometric detector	permeation tube[a]
nitric oxide, nitrogen dioxide	Columbia Scientific Instruments, Mdl 1003-AH	chemiluminescence	gas-phase titration[b]
ozone	Bendix, Mdl 8002	chemiluminescence	gas-phase titration[b]
carbon monoxide	Ford Aerospace	gas filter, correlation	standard gas cylinder

[a] From Stevens et al. (*12*). [b] From Rehme et al. (*13*).

Throughout the study, no vehicles or engines were operated closer than 60 m to the sampling site.

Gas Measurements. The mobile laboratory was equipped with a gas-sampling manifold and instruments for continuous measurement of sulfur dioxide (SO_2), ozone (O_3), nitric oxide (NO), nitrogen dioxide (NO_2), and carbon monoxide (CO). Details of instrumentation used to monitor these pollutants are given in Table I. All the gas monitors are commercially available except the CO monitor. This monitor is based on infrared absorption and was designed by Burch et al. (*10*) for high sensitivity (20 ppb minimum detectable limit) and specificity. Specificity is achieved by the use of a rotating gas filter cell as described by Chaney and McClenny (*11*). Multipoint calibrations of all instruments were performed just before the study; zero and span checks were made daily (*12, 13*). For the CO monitor, calibrations were made at more frequent intervals to account for residual instrument drift during ambient temperature excursions.

Ambient air samples for analysis of volatile organic compounds were collected in 20-L Tedlar (DuPont 2-mil poly(vinyl fluoride) film) bags which were covered with 5-mil black polyethylene to protect the samples from sunlight during collection and storage. Samples were introduced into the bags by pulling outside air through a clean metal bellows pump coupled to the bag through a Swagelock quick-fit connector. After the bags were filled, they were stored in a cardboard box and taken by commercial airlines to Houston, TX. Analysis was then immediately performed by using gas-chromatographic procedures described by Seila (*14*). The maximum storage time between sampling and analysis was 94 h.

Aerosol Measurements. To enable a variety of chemical components to be measured, we collected aerosol samples in three separate dichotomous samplers. Two of these were automated dichotomous samplers (A and B) designed by Loo et al. (*15*) for collecting particles in the 0–2.4- and 2.4 ~20-μm aerodynamic diameter size ranges. The filters consisted of highly efficient 1-μm pore size Teflon membranes of 37-mm diameter mounted on 5-cm square plastic frames and were obtained from Ghia Corp., Pleasanton, CA. To measure daytime and nighttime conditions, we changed filters in the automated dichotomous samplers at 06:30 and 18:30 EST. A Model 200 dichotomous sampler manufactured by Sierra Instruments, Inc., Carmel Valley, CA, was the third sampler (C) used; it collects particles in 0–2.5- and 2.5 ~15-μm ranges. The filters were 37-mm diameter quartz, type 2500 QAST, manufactured by Pallflex Products, Corp., Putnam, CT, and were changed every 24 h.

Table II presents a summary of aerosol sampling conditions and analyses performed. The flow rates indicated in Table II were measured at the inlet of each sampler by using a Model S110 dry test meter made by Rockwell Manufacturing Co. The sampling flow rates and volumes are presented in actual conditions; no pressure correction has been made, even though the average barometric pressure at our sampling site was ~7% lower than the value at sea level. The flow fractions listed in Table II represent that portion of the sampled air flow which passed through the coarse-particle filter in each dichotomous sampler. Using the known value for the flow fraction and the equations given by Dzubay et al. (*16*), we accurately corrected the data for fine–coarse mixing effects.

No attempt was made during sampling to prevent neutralization of collected acid aerosol particles by gaseous ammonia. However, to prevent neutralization by ammonia after sampling, we removed the Teflon filters from the samplers at the end of each sampling period and placed them in a glass chamber that contained ~50 g of H_3PO_3 crystals. The glass chamber also contained several ammonium sulfate controls and sulfuric acid controls, which were prepared in the laboratory by generating aerosols of pure $(NH_4)_2SO_4$ and H_2SO_4 before the field experiment. The quartz filters were stored in 50-mm diameter plastic petri dishes that were lined with aluminum foil. All samples were stored at ambient temperature, ~20 °C. Table II indicates the lengths of time that the samples were stored.

At the end of the field study, the samples were returned to our laboratory. The aerosols collected in sampler A were first analyzed for acidity by exposing the filters to a vapor consisting of ^{14}C-labeled trimethylamine and by counting the β-rays emitted by the ^{14}C retained on the filter (*17*). The method was standardized by using some of the H_2SO_4 control samples described above. When the β-ray counting was complete, the samples were rendered nonradioactive by exposing them to ammonia vapor for a few minutes. Through an exchange reaction, the ammonia molecules replaced the trimethylamine bound to the sulfate in the samples. Next, the samples were analyzed for mass by using β-ray (^{147}Pm) attenuation in an automated instrument developed by Goulding et al. (*18*). Because of the prior exposure to ammonia, any sulfate in the samples would be in the form of ammonium sulfate when the mass analyses were done. The samples were then analyzed for elements with atomic numbers in the range 13–56 (aluminum to barium) and also 82 (lead) by using an energy dispersive X-ray fluorescence (XRF) spectrometer developed by Jaklevic et al. (*19*). Our method for calibration and analysis has been previously published in detail by Stevens et al. (*20*) and by Dzubay and Rickel (*21*).

Filters representing the fine-aerosol fraction collected in

Table II. Summary of Aerosol Sampling Conditions and Analyses

sampler	filter medium	deposit diam, mm	flow rate, L/min	flow fraction[a]	duration, h	analyses	storage time, days
A	Teflon	30.5	52	0.05	12[b]	acidity	3–9
						mass	16–22
						elemental	17–23
B	Teflon	30.5	52	0.05	12[b]	H^+, NH_4^+, NO_3^-, SO_4^{2-}	6–12
C	quartz	29.5	16.7	0.10	24[c]	organic carbon	110
						elemental carbon	110

[a] This represents the fraction of the sampled air flow which passes through the coarse-particle filter in the dichotomous sampler. [b] Sampling periods began at 06:30 and 18:30 EST. [c] Sampling periods began at 18:30 EST.

sampler B were extracted in 20 mL of aqueous solution by using a technique described by Stevens et al. (*20*). Hydrogen ion concentration (H^+) was determined by potentiometric titration (*20*, *22*) on 5 mL of sample extract; ammonium ion (NH_4^+) concentrations were determined by ion selective electrode on 7 mL of sample extract; and sulfate (SO_4^{2-}) and nitrate (NO_3^-) concentrations were determined on 2 mL of sample extract by ion chromatography (*20*, *23*).

Fine-fraction aerosols collected on quartz filters in sampler C were sent to Oregon Graduate Center where they were analyzed for organic carbon and elemental carbon by a method developed by Johnson and Huntzicker (*24*). The reported organic portion is the amount of carbon released in a helium atmosphere at a temperature of 580 °C; the elemental portion is the amount of additional carbon released by combustion when oxygen is added. Tests of this method by Johnson and Huntzicker have shown that soot and several types of organic compounds are analyzed with nearly 100% efficiency, and no crossover between organic and elemental modes could be detected (*24*). If carbonate is present, it will appear as organic carbon, causing the latter to be overestimated.

Gaseous and Particulate Nitrate Measurements. The experimental method has been designed to discriminate between gaseous HNO_3 and particulate nitrate and to avoid ambiguities due to sampling artifacts and is described in detail by Shaw et al. (*25*). Briefly, two sampling systems are run side by side. Each consists of a Teflon particle filter followed by a nitric acid collecting tube made from Teflon and packed with nylon fibers. One sampling system is preceded by a gas diffusion denuder (*20*) for removal of HNO_3 gas. Except for the denuder and the nylon in the tube, the sampled air stream is exposed only to Teflon. One determines the net atmospheric HNO_3 concentration by taking the difference in total nitrate sampled by the two systems running simultaneously.

The filter samples were analyzed by wet chemical extraction and ion chromatography for NO_3^-. Nylon collection tube samples were analyzed for HNO_3 by a technique developed by Tesch (*26*). This technique consists of washing the collected HNO_3 from the tube with aqueous NaOH, adding benzene and concentrated H_2SO_4, and analyzing the resulting nitrobenzene by gas chromatography.

Artifact Formation on Glass Fiber Filters. Glass fiber filters from a batch of hi-vol filter media purchased from Whatman, Ltd., under EPA contract no. 68-02-1756, were placed in a sampling system in which the glass fiber filter was preceded by a Teflon filter and all upstream parts of the system were made of Teflon. The intent was to collect atmospheric particles on the Teflon filter and permit gases to pass through to the glass filter. The filter area and the flow rate were such that the same face velocity that occurs during operation of a hi-vol was produced for this sample. These filters were analyzed for SO_4^{2-}, NO_3^-, and carbon.

Results and Discussion

Gas Measurements. Table III lists the 24-h average ambient concentrations of O_3, NO, NO_2, SO_2, and CO measured from the mobile laboratory at the Elkmont monitoring site. Values in parentheses are the maximum values of the distribution of 1-h averages.

The ozone concentrations followed a typical photochemical pattern, rising in the midmorning to levels between 40 and 80 ppb and then falling in late afternoon to concentrations below 10 ppb and remaining low through the night. An exception to this pattern occurred on September 21 at 22:00, when the O_3 concentration rose to 70 ppb simultaneously with the onset of a thunderstorm. After the storm, the O_3 concentration gradually fell and reached 10 ppb at 08:00 on September 22.

Throughout the study, considerable short-term (several minutes) fluctuations in O_3 concentrations were observed. The fluctuations occurred too rapidly to be explained by variation in cloud cover and were apparently due to intrusion of air containing reactive species.

The NO and NO_2 concentrations were typically below 5 ppb and showed no long-term trends. A few, rare short-term peaks of several minutes' duration, however, ranged as high as 70 and 60 ppb for NO and NO_2, respectively. These peaks generally occurred during the daylight hours and were visually associated with local vehicular traffic. Peaks in NO concentration were correlated with short-term reductions of O_3 concentrations during the day.

Table III shows that 24-h average levels of CO did not exceed 400 ppb. Carbon monoxide events ranged from 100 to 850 ppb and did not exhibit a typical urban diurnal pattern. Two types of CO events were observed: (1) long-term events lasting a few hours and occurring no more frequently than once a day and (2) short-term events lasting a few minutes and occurring as many as 100 times a day. We believe that the short-term events were caused by passing automobiles. Long-term CO events occurred during 09:00–11:00 on September 22 and during 18:00–24:00 on September 23, when concentrations rose from 300 to 850 ppb. The CO events on September 22 were accompanied by increases in Freon 11 and Freon 12 concentrations (*9*), but the second CO event did not show a corresponding increase in halocarbon concentration. Hence the two air masses passing through the sampling site during these times had different geographic origins (to be discussed later in the text). The daily short-term CO events were clearly anticorrelated with large, short-term decreases in O_3, strongly suggesting that NO from automobiles traveling through the park was responsible. Concentrations of NO were often below detection limits, so that direct comparison of CO with NO was not possible.

Table III. 24-h Averages and Maximum 1-h Averages: Elkmont Site, Great Smoky Mountains

	concn, ppb				
date	O_3	NO	NO_2	SO_2	CO
9/21/78	38 (70)[a]				<400[b]
9/22/78	37 (70)	<5[c]	<5[c]	3[b] (4)[a]	<400
9/23/78	19 (55)	<8	<11	8 (10)	<370
9/24/78	18 (40)	<6	<7	10 (10)	<170
9/25/78	30 (25)	<4	<4	11 (15)	<190
9/26/78	18[d] (25)			15[e] (18)	<190[d]

[a] Values in parentheses are maximum 1-h averages. [b] 16:00–24:00. [c] 18:00–14:00. [d] 01:00–07:00. [e] 01:00–17:00.

Table IV. Average Volatile Organic Composition of Great Smoky Mountain Air for September 25 and 26, 1978

	concn, ppb carbon	
organics, class	9/25/78[a]	9/26/78[b]
paraffins	42	55
olefins	9	17
aromatics	18	24
oxygenates	13	13
unknown[c]	15	16
acetylene	3	7
total volatile organic compounds	100	132

[a] Averages for the following sampling periods: 06:00–08:00, 10:00–10:20, 12:00–12:15, 14:15–14:45, 16:00–16:20. [b] Averages for the following sampling periods: 08:25–08:27, 08:30–08:38, 10:00–10:20, 11:30–11:35. [c] Unidentified peaks.

Table IV is a summary of the results of volatile organic compounds measurements made on September 25 and 26. Details of the individual hydrocarbons measured in each period are included in a report by Arnts and Meeks (*27*). These investigators concluded that most of the volatile organic compounds measured were emitted by vehicular traffic, with no more than 6% of the total organic mass measured produced by biogenic emissions. The biogenic contribution was estimated by measuring the amount of isoprene and α-pinene present in the samples. In the nine samples, the highest isoprene concentration (which was the dominant terpenoid species) measured was 6 ppbC.

Aerosol Measurements. Several features are apparent in the results (Table V) of the average mass and composition of aerosols collected with dichotomous samplers A and C. First of all, only ~20% of the total mass occurs in the coarse fraction, in contrast to ~36–57% previously reported by Stevens et al. (*20*) for several urban areas. The relatively low coarse-particle mass observed in the Great Smoky Mountains may be due to factors that tend to minimize the suspension of coarse-particle dust such as the abundance of foliage and the lack of major anthropogenic activities. A second feature of Table V is that 95% of the sulfur occurs in the fine fraction, with sulfur accounting for 16% of the fine-fraction mass. We will show below that sulfur and its associated cations account for 61% of the fine-fraction mass. In our previous study of urban areas (*20*), sulfur was not so highly abundant in the fine fraction. The most surprising feature in Table V is the low abundance of carbon in the aerosol. Organic carbon accounts for only 9% of the fine-particle mass. Similar results were obtained by Pierson et al. (*8*) for a study conducted during the summer of 1977 on a forested mountain in southwestern Pennsylvania.

Table V. Mass and Elemental Concentrations for Average Daytime, Average Nighttime, and Average for All Samples Collected at Elkmont, TN, between September 20 and 26, 1978

	fine, ng/m^3			coarse, ng/m^3		
	day	night	mean	day	night	mean
Mass	26400	22000	24000	6200	4900	5600
C (organic)			2200			1200
C (elemental)			1100			<100
Al	25	15	20	258	200	195
Si	48	27	38	762	399	580
S	4145	3344	3744	194	214	204
Cl	<10	<10	<10	9	5	7
K	38	42	40	118	98	108
Ca	19	12	16	459	186	322
Ti	<2	<2	<2	27	9	18
V	<2	<2		<2	<2	<2
Fe	29	26	28	166	70	118
Ni	1	1	1	2	2	1
Cu	3	3	3	<3	<3	<5
Zn	8	10	9	<3	<3	<4
As	2.5	2	2.2	<1	<1	<1
Se	1.5	2.3	1.4	0.2	0.2	0.2
Br	11	7	18	7	2	5
Pb	126	68	97	22	6	14

Table VI. Ionic Composition and Sulfur Concentrations in the Fine Fraction by Two Different Methods

		acidity, [a]	ionic composition, [b] nequiv/m^3				sulfur, ng/m^3	
day	time	nequiv/m^3	H^+	NH_4	NO_3^-	SO_4^{2-}	IC [b]	XRF [a]
20–21	18:30–06:30	94	80	143	<6	193	3090	3330
21	06:30–18:30	112	113	189	<6	333	5330	4400
21–22	18:30–06:30	105	81	155	<6	227	3630	3740
22	06:30–18:30	145	169	170	<6	360	5760	4620
22–23	18:30–06:30	63	58	74	<6	130	2080	2100
23	06:30–18:30	90	77	88	<6	172	2750	2720
23–24	18:30–06:30	90	62	107	<6	175	2800	2720
24	06:30–18:30	90	90	75	<6	172	2750	2810
24–25	18:30–06:30	95	108	100	<6	211	3380	3450
25	06:30–18:30	201	196	119	<6	351	5620	5360
25–26	18:30–06:30	164	158	148	<6	332	5310	4730
26	06:30–18:30	171	174	152	<6	341	5460	4960
blanks [c]			0.8 (0.9)	0.3 (2)	<6	0.6 (2)		5 (2)
H_2SO_4 controls [c]			65 (13)	20 (7)	<6	78 (9)		
H_2SO_4 controls [c]		105 (57)						1310 (70)
$(NH_4)_2SO_4$ controls [c]		3 (3)	−0.1 (0.6)	43 (4)	<6	48 (3)		110 (24)

[a] Acidity and sulfur are measured on aerosol collected in sampler A by using amine exposure method and XRF method, respectively. [b] Ionic composition measured on aerosol collected in sampler B. [c] The average values for blanks and controls are computed by assuming that the sampling volume is 34 m^3. Standard deviations are shown in parentheses.

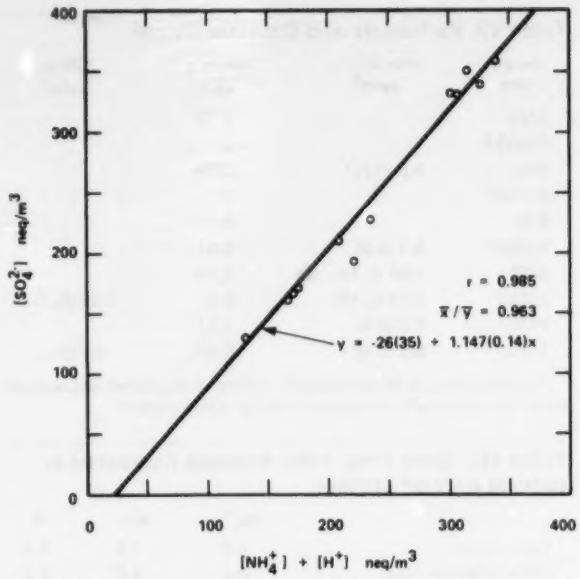

Figure 1. A test of charge balance showing anion vs. cation concentrations. The numbers in parentheses are 95% confidence intervals for the linear regression coefficients.

Such findings contradict the hypothesis that products of terpenes derived by photochemical oxidation account for a major portion of the fine-particle aerosol mass in forested areas.

Table VI shows the ionic composition and the sulfur concentrations measured for fine particles collected in two different dichotomous samplers. In comparing the sulfur measured by XRF with sulfur values from ion chromatographic sulfate measurements, one finds that the correlation coefficient is 0.97 and the ratio of the averages is 0.94 (XRF/ion chromatography). Since the sulfur calibration of the XRF is accurate to ~8%, the ratio is equal to unity within experimental error and is consistent with the notion that sulfur is entirely in the form of sulfate. The data in Table VI on ionic composition indicate that a negligible amount of nitrate was collected on the Teflon filters.

Figure 1 is a plot of sulfate vs. the sum of the ammonium and hydrogen ion concentrations. The ion concentrations are plotted in units of nequiv/m^3 to enable testing of the ion charge balance. The linear regression has a 95% confidence interval for the intercept that overlaps zero and a 95% confidence interval for the slope that nearly overlaps unity, which indicates that the sulfate occurs as varying proportions of $(NH_4)_2SO_4$, NH_4HSO_4, and H_2SO_4.

Figure 2a is a time-series plot of H^+ and NH_4^+ molar concentrations. It is apparent that during the early portion of the study there is more NH_4^+ than H^+. During the later portion the reverse is true.

The relative purity of H_2SO_4 in the aerosol can be estimated from the ratio

$$f = \frac{[H^+]}{[H^+] + [NH_4^+]}$$

This ratio would have values of 0, 0.5, and 1 for $(NH_4)_2SO_4$, $(NH_4)HSO_4$, and H_2SO_4, respectively. From the data in Table VI, the ratio f has a mean value of 0.47 and a standard deviation of 0.09. The minimum value is 0.34, and the maximum is 0.62. All of the samples were therefore acidic, and the average acidity is close to that of ammonium bisulfate (NH_4HSO_4). Such results pertain to the average composition of all particles but not necessarily to the composition of individual particles.

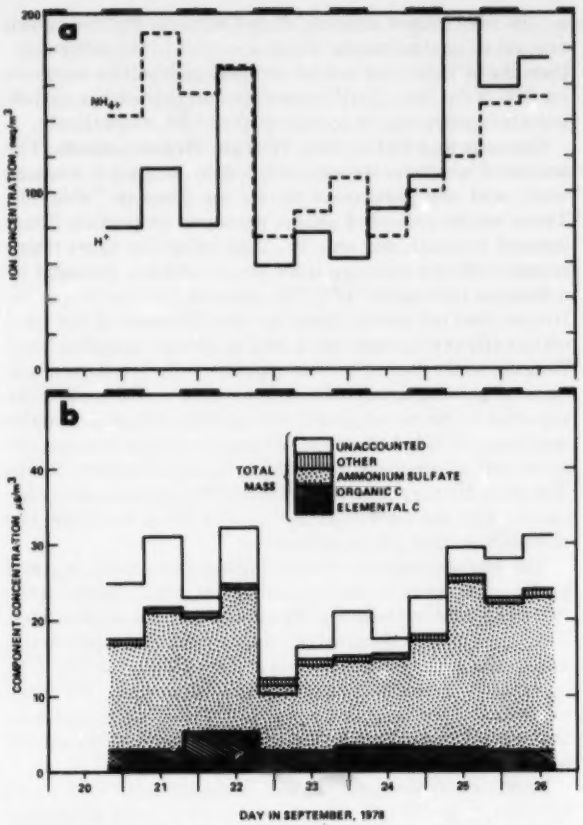

Figure 2. Time-series plot for the fine fraction showing (a) H^+ and NH_4^+ ionic concentrations in nequiv/m^3 and (b) total fine-particle mass and its various components. The component labeled "other" includes crustal matter and the noncarbonaceous portion of vehicle exhaust aerosol.

How well do these laboratory analyses correspond to the true average acidity of the aerosol particles as they existed in the atmosphere? The data on the ammonium sulfate controls in Table VI show that pure ammonium sulfate standards were not made acidic during storage in the dry, ammonia-free chamber. However, the supposedly pure H_2SO_4 controls were ~24% neutralized. In addition, some neutralization of the collected ambient aerosols could have taken place during sampling. In previous studies in which acidity was measured, we used a diffusion denuder at the sampler inlet to remove ammonia during sampling (*17, 20*). However, no denuder was used for the present measurements in the Great Smoky Mountains. Thus the aerosols could have been even more acidic than the data in Table VI and Figure 2a indicate. However, our acidity values for the Great Smoky Mountains are similar to those obtained by Pierson et al. in a study of aerosols in a forested mountain area (*8*).

Figure 2b is a time-series plot showing mass and the major components in the fine fraction. Because all of the acidity was deliberately neutralized by ammonia before mass was measured, the sulfate is shown as ammonium sulfate. It is clear that the mass in the fine fraction is dominated by the sulfate component. An interesting feature of both Figure 2b and Table V is that the mass and sulfur tend to be higher in the daytime than at night. Moreover, according to Figure 2a, the acidity always increases during the daytime. Such diurnal effects were not seen in the study of aerosol in a forested mountain area by Pierson et al. (*8*).

As noted above, sulfate and its associated cations represent the major component of the fine fraction. Ammonium sulfate accounts for 64% of the average fine-particle mass measured

on the neutralized samples. If one corrects for the known amount of neutralization which occurred in the laboratory, then the original acid sulfate ammonium bisulfate accounts for 61% of the fine-particle mass, and organic carbon and elemental carbon only account for 10 and 5%, respectively.

Gaseous and Particulate Nitrate Measurements. The analytical results for the sampling system designed to measure nitric acid and particulate nitrate are given in Table VII. These results consist of nitrate measured on particle filters (second column), and on nitric acid collection tubes (third column) for two sampling lines, one of which is preceded by a denuder (subscript "D"). The gaseous nitric acid concentration (last column) is given by the difference of the total nitrate (filter plus tube) measured in the two sampling lines. Because of the loss of several samples, only two determinations of gaseous nitric acid were successful. Because of the variation in blank values and because the diffusion denuder may have excluded nitrate in the coarse-particle fraction, the nitric acid determinations should be regarded as upper limits. The denuder may have excluded coarse particles simply because their inertia would not permit them to follow the streamlines through the apparatus.

The total atmospheric nitrate due to gaseous nitric acid and particulate nitrate is given by the sum of nitrate found on the filter and tube in the sampling system without the denuder. The range is 0.5–1.3 $\mu g/m^3$ of total nitrate. The total *particulate* nitrate is given by the sum of nitrate found on the filter and tube in the sampling system with the denuder. The range of particulate nitrate is 0.1–0.4 $\mu g/m^3$. This is consistent with the results of analyses of dichotomous sampler filters reported in Table VI.

For completeness, analyses were also carried out for the ions H^+, NH_4^+, and SO_4^{2-}. These results are in good agreement with those from the more extensive dichotomous sampler measurements presented in Table VI. The average values of SO_4^{2-} and NH_4^+ are 11 and 2.3 $\mu g/m^3$, respectively. The stoichiometric ratio of $(H^+ + NH_4^+)/SO_4^{2-}$ is unity within experimental error, consistent with the interpretation that atmospheric sulfate is present as a mixture of H_2SO_4, NH_4HSO_4, and $(NH_4)_2SO_4$. Because of the very small relative amount of NO_3^-, this species can be neglected in determining stoichiometric ratios.

Artifact Formation on Glass Fiber Filters. Although glass fiber filters were not used to obtain any of the data reported in the other sections of the paper, an experiment was performed to determine artifact formation on glass fiber filters. An air-quality standard based on the mass of inhalable particles (those with aerodynamic diameter less than 15 μm) is under current consideration by EPA, and glass fiber filters are possible collection media. The properties of glass fiber filters must therefore be examined under a variety of atmospheric conditions. This experiment was designed to determine the extent of artifact formation caused by reaction of gases with glass fiber filters. Previous experiments in urban areas have shown significant formations of sulfate and nitrate due to reactions of gases on glass fiber filters used in hi-vol samplers (*28*).

The glass fiber filters were analyzed for SO_4^{2-} and NO_3^- by using wet chemical extraction and ion chromatography, and for carbon by using a combustion technique. The results are given in Table VIII. The 95% detection limit is based on the analytic reproducibility of blank filters and is defined such that 95% of the observations at that level correspond to valid samples above the blank. Four samples, labeled by date, were taken during the study. In Table VIII, "net sample" refers to analytic results from which the blank values have been subtracted. We conclude from the results that formation of artifact carbon and sulfate has occurred on the glass fiber filter and, based on the sampling rate which would be equivalent to operation of a hi-vol sampler, the values correspond to 0.7–2.2 $\mu g/m^3$ of sulfate and 0.3–1.1 $\mu g/m^3$ of carbon. The variation in the blank does not permit the quantitative determination of nitrate artifact. These conclusions involve the assumption that the particles collected on the Teflon filter did not release gases that, in turn, reacted on the glass fiber filter. Pierson et al. (*29*) carried out a study of artifact formation on filters of sulfate, nitrate, and hydrogen ion on a forested mountain in southwestern Pennsylvania. They found a significant correlation between ambient SO_2 and sulfate artifact on glass fiber filters.

Table VII. Particulate and Gaseous Nitrate

sample date	filter NO_3^-, $\mu g/m^3$	tube NO_3^-, $\mu g/m^3$	HNO_3, $\mu g/m^3$
9/20		0.05	
9/20D[a]		0	
9/21	0.6 (0.7)[b]	0.09	
9/21D[a]		0	
9/22		0.11	
9/22D[a]	0.1 (0.2)	0.01	
9/23	0.35 (0.18)	0.13	
9/23D[a]	0.14 (0.18)	0.01	0.33 (0.25)
9/25	1.2 (0.4)	0.12	
9/25D[a]	0.4 (0.4)	0.03	0.9 (0.6)

[a] Sampling line with diffusion denuder. [b] Standard deviation of measurement (based on variance of large number of quality control checks).

Table VIII Glass Fiber Filter Artifacts Expressed in Units of $\mu g/cm^2$ of Filter

	SO_4^{2-}	NO_3^-	C
blank values	0.5	1.2	5.9
95% detection limit[a]	0.2	3.2	2.2
net sample values/area filter			
9/20	4.7	0.0	4.6
9/21	15.8	2.0	11.2
9/23	9.2	4.8	4.0
9/25	12.3	2.4	1.3

[a] Based on standard deviations of the blank.

Airmass Trajectory Data. Parkhurst (*30*) computed 24-h back trajectories for six cities (Birmingham, AL, Nashville and Knoxville, TN, Greensboro, NC, Columbia, SC, and Atlanta, GA from National Weather Service 24-h data). These back trajectories are the numerical averages of those for 1000 mbar (representing surface trajectories) and for 850 mbar (representing trajectories at 1525 m) obtained from routinely generated National Weather Service prognostic models. The data of Parkhurst indicate that the air masses which reached the Great Smoky Mountains during the period of our study originated from a wide variety of directions and locations. We attempted to find a relationship between particulate sulfate concentration and 24-h trajectory direction but could discern none. Therefore the sulfate which reaches the Great Smoky Mountains did not originate from a single nearby source. Because sulfate can persist in the atmosphere for 4 days or more (*31*), a variety of nearby and distant sources can contribute to the aerosol in the Great Smoky Mountains.

Airborne Measurements over Sampling Site. Airborne measurements of O_3 and SO_2 concentrations were measured from a Cessna 337 Skymaster twin-engine airplane owned and operated by the Civil Engineering Department of Virginia Polytechnic Institute, Blacksburg, VA. The airplane was equipped with a Meloy chemiluminescence O_3 monitor and a Meloy 285 flame photometric detector for sulfur dioxide.

Details of the instruments and operation have been described by Stephens et al. (*32*).

Measurements over the sampling site were made between 15:02 and 15:05 on September 25. At elevations between 760 and 1130 m MSL (mean sea level), ozone concentrations remained relatively constant, ranging from 49 to 85 ppb, while the sulfur dioxide concentration was less than 10 ppb. Between 15:02 and 15:05 on the ground at the sampling site, ozone and sulfur dioxide concentrations averaged 70 and 14 ppb, respectively.

Airborne collection of aerosols on Teflon filters was carried out for short periods on September 21, 22, 25, and 26. Aerosol composition was determined by using XRF for sulfur, ion selective electrode for ammonium ion, and Grans titration for hydrogen ion. During the periods sampled, the sulfate concentrations ranged from a minimum of 8 to a maximum of 20 $\mu g/m^3$, with the sulfate present as some combination of $(NH_4)_2SO_4$, NH_4HSO_4, and H_2SO_4, indicating that the air mass at the monitoring sites contained the same aerosol sulfate species as measured in flight.

Haze and Aerosol Acidity. The haze-producing characteristic of an aerosol comes about through the aerosol's fundamental physical properties of refractive index, size distribution, and particle number concentration. The chemical properties of the aerosol are important insofar as they determine the refractive index and the change in size distribution when the aerosol is exposed to varying relative humidity. The laboratory investigations of Charlson et al. (*33*) on the characteristic differences in light scattering by aerosols of $(NH_4)_2SO_4$, NH_4HSO_4, and H_2SO_4 under conditions of increasing humidity suggest the importance of the degree of acidity in determining the haze-producing potential of sulfate aerosols. In those measurements for $(NH_4)_2SO_4$, there was virtually no increase in light scattering with increasing humidity until values greater than 70% were reached. By contrast the light scattering by the two more acidic (and hygroscopic) forms of sulfate increased by a factor of 2–3 as relative humidity was increased between 50 and 80%.

In the present study a large portion of the fine-particle aerosol mass was determined to be composed of NH_4HSO_4 and, possibly, H_2SO_4. Further, the daytime relative humidity was generally above 60%. While it is tempting to speculate that the concurrence of both humidity and acidity may cause an increase in haze over that which would be estimated from the total fine-particle mass concentration (*34*), no quantitative measurements of visibility were performed to examine this possibility. It is important to note however that in a field measurement in which relative humidity decreases as well as increases, the phenomenon of hysteresis (*35*) may lessen the difference between the light-scattering properties of the two classes of sulfate aerosols. When the relative humidity to which a droplet of pure $(NH_4)_2SO_4$ is exposed is gradually decreased below its deliquescence humidity (80%), the water content of the droplet decreases, but not abruptly. At a given humidity (between the deliquescence humidity and the much lower "crystallization" humidity) the water content of the droplet remains well above the value it would have had if the humidity were instead increasing from a very low value. It is quite common for ambient humidity to cycle above and below 80% relative humidity with a diurnal variation, so that ambient $(NH_4)_2SO_4$ aerosol may well exist more often in a state of high water content—and consequently with enhanced light-scattering ability—than with the low water content appropriate to the results of Charlson et al. (*33*).

In passing we note that Husar and Patterson have analyzed trends in visibility in the eastern United States between 1948 and 1974 (*36*). They report a large decrease in visibility for the summer months, July through September, and find that this trend coincides with a trend toward increased coal consumption during summer months. For the region surrounding the Smoky Mountains the decrease in summertime visibility was very substantial.

A final qualitative observation was our perception of the visible haze as white during the period of our study, independent of viewing angle. There was no indication of the blue haze which Went described previously (*1*).

While the present study does not provide any quantitative results relating aerosol acidity and visibility, it is hoped that the high acidity levels which have been measured in the study will encourage future investigation of its effects on visibility.

Conclusions

Organic compounds and inorganic pollutant gases associated with industrial and automotive emissions dominated the gaseous pollutants in the atmosphere. For the period when organics were measured, volatile gas-phase organics did not exceed 132 ppb carbon, and biogenic emissions contributed less than 6 ppb carbon to the organics measured.

Aerosol measurements made in the Great Smoky Mountains revealed that sulfate and its associated cations represented 61% of the fine-particle mass. The average ionic composition of the SO_4^{2-}, H^+, and NH_4^+ was equivalent to ammonium bisulfate. Of the total mass measured in fine particles, elemental carbon accounted for 5% and organic carbon accounted for 10%. Crustal elements such as aluminum, calcium, iron, and silicon were minor constituents of the fine-particle mass. This work shows that during the period of the study the fine-particle aerosol in the Great Smoky Mountains was dominated not by natural organic compounds but by acid sulfates.

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